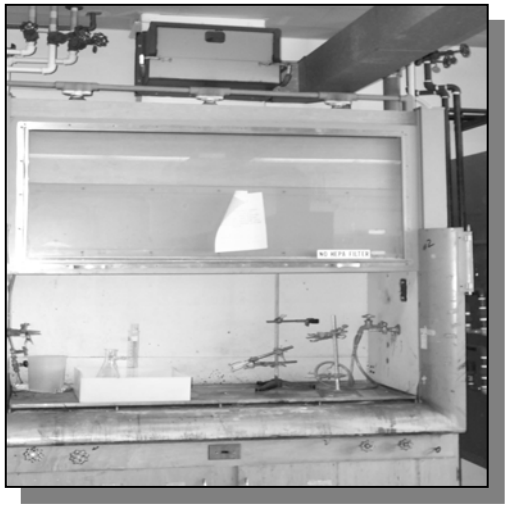
Perchlorate and Perchloric Acid Sampling and Analysis Procedure

Content



1.0 Purpose/Scope

This document describes a field procedure for taking and analyzing wipe samples of surfaces potentially contaminated with perchlorates from perchloric acid use. It is based on methodology described *in Perchloric Acid Contaminated Hood Decontamination Procedure Manual* (1993), prepared by ORNL. The goal of the procedure is to provide a uniform method to collect representative samples of surface contamination (such as lab hoods and duct work) and to provide a standardized, accurate method to analyze the concentration. Using this method will ensure repeatability between various sampling personnel and surface configurations.

This field procedure describes practices developed from lessons learned experience. This procedure should be viewed as a best management practice. Regulatory limits for surface contamination with perchlorates do not exist, but this method allows quantification of surface levels for comparison with known safe levels from industry experience.

2.0 Responsibilities

2.1 This program is implemented through the SHSD Industrial Hygiene Group Leader who may delegate authority to administer this program. Members of the SHSD Industrial Hygiene Group can be qualified to perform certain tasks in this program. Personnel who

have demonstrated competency in performing a certain role, in accordance with Section 7 of this procedure, will be qualified to serve that role.

2.2 Chain of Custody procedures: The collector of the sample is responsible for the integrity of the sample until the sample has been properly transferred to the IH Group laboratory using the SHSD IH 51300 *Chain of Custody* procedure. It is permissible to use this procedure to collect samples that will be analyzed by a laboratory not associated with the SHSD IH Group.

2.3 Hazard Analysis of the Sampling Task: It is the responsibility of the person using this method and his/her supervisor to ensure that the appropriate personal protective equipment is worn while performing this procedure. In addition, the person performing this procedure and his/her supervisor are responsible to ensure that all required training and qualification for hazards that may be present in areas where this procedure will be used (such as respiratory protection or radiation contamination) have been met. The person performing this procedure and his/her line supervisor are responsible to comply with all work planning and work permit system requirements.

3.0 Definitions

- ***Perchlorate(s):*** Compound containing a monovalent $^{-}ClO_4$ radical, including salts of perchloric acid, such as Ammonium perchlorate and magnesium perchlorate. Unstable material, flammable by chemical reaction, powerful oxidizer, explosive hazard when shocked, exposed to heat, or chemical reaction.
- ***Perchloric Acid:*** Colorless, fuming, unstable liquid, severe explosion hazard, $ClH0_4$.
- ***Qualified Sampler****:* A person who has demonstrated competency, in accordance with Section 7, to perform this field procedure.
- ***Qualified Analyzer****:* A person who has demonstrated competency, in accordance with Section 7, to perform this analysis procedure.

4.0 Prerequisites

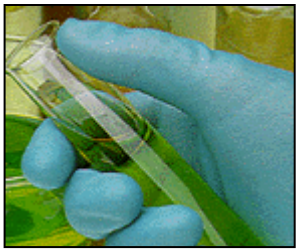
Only persons who have demonstrated competency to the satisfaction of the SHSD IH Group Leader or designee will be qualified to perform work under this SOP. The qualification criteria to perform this procedure are established in Section 7.

5.0 Precautions

5.1 **Personal Protective Equipment**:

5.1.1 **Sampling:** Appropriate personal protective equipment to protect the person collecting the sample must be used when implementing this procedure.

- At a minimum, use disposable gloves when contacting the surface material and handling exposed sampling media. The gloves must have sufficient impermeability to the surface contaminant and solvent used on the collection media to allow safe handling. Recommended gloves are disposable Nitrile, Natural Latex Rubber, or PVC.
- Where the potential for contamination of the body can occur, use disposable clothing to cover the areas of contact.
- Use Ballistic gear (riot helmet, face shield, and flack jacket) in duct sampling, when the sampling will result in a shock hazard to the duct work.
- When sampling interiors of lab hoods, use the sash as a barrier between the sampler and surface being tested to the greatest extent possible.



5.1.2 **Analysis:** Disposable gloves must be used when mixing the 70% Perchloric acid and should be used when handling the glassware and pipettes containing diluted perchlorates. Recommended gloves are disposable Nitrile, Natural Latex Rubber, or PVC. Use safety glasses and a lab coat. Be sure the perchloric acid does not contact organic material.

5.2 **Radiation Contamination:** It is possible that some surfaces to be tested may have radiation contamination as well as the chemical contamination. In these cases, personal protective equipment and administrative controls must be implemented for the radiological contaminant hazard in addition to the chemical hazard. In addition, the collected sample must be analyzed for the radiological hazard, where appropriate, before it can be submitted to the IH Group for analysis of metal or chemical concentration. At no time will the IH Group accept a sample with radiological contamination above permissible limits for the general public.

5.3 **Work Planning:** All requirements of work planning system must be met in performing this procedure.

5.4 **Perchlorate Hazard:** Crystals of perchlorates, when dry, pose an explosion hazard when disturbed. The bottle containing the 70% solution of Perchloric Acid should be kept moist at all times

to prevent the formation of perchlorates at the interface of the bottle and cap. To achieve this, the acid bottle is stored within a second bottle containing a moist paper towel.

6.0 Procedure

Equipment

Sampling Equipment

6.1.1 PPE listed in Section 5.1.
6.1.2 4x4 inch cotton gauze or equivalent
6.1.3 Rod or extension device
6.1.4 Distilled water
6.1.5 Sample containers
6.1.6 Rubber bands (to hold gauze or pad to extension devise)

Analysis Equipment

6.1.7 PPE listed in Section 5.1.
6.1.8 Ion selective electrode testing kit
6.1.9 Water sprayer
6.1.10 Suction pump or equivalent equipment
6.1.11 Tygon tubing
6.1.12 Flasks
6.1.13 2M Ammonium Sulfate solution (See 6.3 for preparation)
6.1.14 Ion Buffer (See 6.3 for preparation)
6.1.15 2000 ppm Perchlorate Stock (See 6.3.4 for preparation)
6.1.16 Orion Model 290A pH/mV meter
6.1.17 Orion dual probes:
- Yellow *Reference* probe
- Black *Perchlorate* probe

Perchlorate Field Sample Collection

6.2 Select appropriate sample locations, including assessable points in hoods, exhaust stacks, and fan housings.

From inside the hood, sample can be taken from:
- Walls of the hood, especially near the back by air flow intakes
- Work surface/Counter top
- Within the upper baffle opening

- Within the lower baffle opening
- Around the mouth of the duct, if accessible.

From the exterior of the system, consider sampling:

- Inside of the duct walls, if openings exists (such as isolation dampers, traverse sampling ports, etc.)
- Around the mouth of the duct at the rain cap.
- Fan Housings (via isolation dampers, service panels, etc.)

6.3 **Sampling a hood, duct, or exhaust stack with a gauze wipe**

6.3.1 Secure a piece of gauze to a wooden rod or other appropriate extension device. A rubber band typically secures the gauzes well.

6.3.2 Moisten the gauze with the distilled water. Gently dab and hold the wetted gauze to surface to be tested. Move over the surface in a dabbing/holding motion. Avoid hard rubbing and shock to surfaces.

6.3.3 Using gloves, remove the gauze and place into a labeled sample container.

6.3.4 Add **25mL** of distilled water.

6.3.5 Shake the vial for at least one minute.

6.3.6 Continue using Step 6.2.2.1 to 6.2.2.5 until all samples are collected.

6.3.7 Proceed to section 6.3 for analysis procedure.

6.4 **Sampling a fan housing or duct with liquid wash down**

6.4.1 Spray about 1 liter of distilled water into the fan housing or exhaust opening (system must be off).

6.4.2 Direct the spray toward the fan while someone slowly turns the fan shaft.

6.4.3 Allow the water to accumulate at the bottom of the fan housing (or in hood as appropriate).

6.4.4 Feed Tygon® tubing into the fan housing until the tube reaches the wash water.

6.4.5 Turn on a suction pump to collect the wash down water. It will provide a sample liquid (sufficient sample volume is 50mL).

6.4.6 Proceed to section 6.3 for analysis procedure.

6.5 **Record sampling information:** Label the container used to collect the sample and complete a Field Survey Form. The label and form should document the following: Date; Building and room identification; Source identification; Location in the exhaust ventilation system where sampled (i.e., hood, fan, stack, etc.); Suspected sample contents—contaminant; Specific location of each sample; Surface Area sampled- estimate (quantify the area, such as 100 cm^2 or 1 square foot.); Samplers name

Perchlorate Laboratory Analysis

6.6 **Ammonium Sulfate solution preparation**

6.6.1 Tare a piece of weighing paper on the balance.
6.6.2 Weight **26.43** +/- 0.5 **grams** of Ammonium Sulfate on the balance.
6.6.3 Dissolve the 26.43g of Ammonium Sulfate (99+% purity) in approximately 50mL distilled water in a 100 ml beaker.
6.6.4 Transfer the solution to a 100mL volumetric flask.
6.6.5 Repeatedly rinse the transfer beaker with distilled water; transfer the rinses to the volumetric flask.
6.6.6 Bring flask up to the **100mL** mark with de-ionized or distilled water.
6.6.7 Stopper the flask and invert several times to mix.
6.6.8 Label flask as ***"2M Ammonium Sulfate"*** with the current date.

6.7 **Ion Buffer solution preparation**

6.7.1 Pipette 2mL of the *2M Ammonium Sulfate Solution* into a 100mL volumetric flask and fill to the mark with distilled water.
6.7.2 Label the flask "***Ion Buffer solution***".

6.8 **Instrument set-up**

6.8.1 **Battery Check:** On the Orion Model 290A pH/mV meter, check the battery status by turning the meter "on" (press the **"Power"** button). Replace the 9V-battery if no display occurs.
6.8.2 **Reference Electrode:** Flush the yellow, double junction reference electrode with distilled water. (Note: Refill each chamber with the appropriate solution before taking measurements.)

- Fill the inner chamber with the manufacturer supplied "***Double Junction Reference Electrode Inner Filling Solution",*** Orion Part Number 900002.
- Fill the outer portion with the ***Ion Buffer Solution*** prepared in Step 6.3.2.

6.8.3 **Specific Ion (Perchlorate) Electrode:** Remove the rubber end-cap from the black *93 Series Electrode* body (if new or dry stored) or remove the probe from its long-term storage distilled water bath.

6.9 **Establishing a Baseline Meter Reading:**

6.9.1 Place both probes approximately 1" to 2" into distilled water in a beaker for 5 to 10 minutes.

6.9.2 Place both probes into a 100 ml beaker containing the ion buffer solution to 1" to 2" depth. Insert a stirring bar and place the beaker and probes on a stirring plate. Spin the bar.

6.9.3 Turn the meter "on". Use the **"mode"** button to select the **"mV"** setting. **If the reading does not stabilize and is NOT greater than 280mV, the Perchlorate probe is "bad" and should be replaced.** Do not proceed with measurements using that probe.

6.9.4 Record the meter reading of the perchlorates in the *Ion Buffer (Pre-Test)* line on the *Perchlorate Analysis Record*.

6.9.5 Rinse the probes with distilled water between solutions.

6.9.6 Place the probes into distilled water and record the mV reading in the *Distilled Water Pre-Test)* line on the *Perchlorate Analysis Record*.

6.10 **Perchlorate Stock solution preparation**

6.10.1 Pipette **0.173mL** of 70% Perchloric acid into a 100mL volumetric flask.

6.10.2 Add distilled water to the **100mL** mark, cap the flask, and invert to mix.

6.10.3 Label as "*2000ppm Perchlorate Stock*" and mark the date on the flask.

6.11 **Calibration Standards preparation**

6.11.1 Calibration Solution 1: Using a volumetric pipette, pipette **0.5mL** of the *2000 ppm-perchlorate stock* into a 50mL volumetric flask.. Add **2mL** of 2M Ammonium Sulfate and fill to the mark with distilled water. Label as "*20 ppm-perchlorate calibration standard*."

6.11.2 Calibration Solution 2: Using a volumetric pipette, pipette **5.0mL** of the 2000 ppm-perchlorate stock into a 50mL volumetric flask. Add **2mL** of 2M Ammonium Sulfate and fill to the mark with distilled water. Label as "*200 ppm-perchlorate calibration standard*."

6.11.3 Calibration Solution 3: Using a volumetric pipette, pipette **10.0mL** of the 2000 ppm-perchlorate stock into a 50mL volumetric flask. Add **2mL** of 2M Ammonium Sulfate and fill to the mark with distilled water. Label as "*400 ppm-perchlorate calibration standard*."

6.11.4 Calibration Solution 4: Add **2mL** of 2M Ammonium Sulfate into a 50mL volumetric flask. Fill to the mark with the *2000 ppm-perchlorate stock* into to the mark. Label as "*2000 ppm-perchlorate calibration standard*."

Final Concentration [ppm]	Volume of "2000 ppm Stock"	Volume of Distilled Water	Volume of 2M Ammonium Sulfate	Total Volume
20	0.5 ml	47.5 ml	2.0 ml	50 ml
200	5.0 ml	43.0 ml	2.0 ml	50 ml
400	10.0 ml	38.0 ml	2.0 ml	50 ml
2000	48.0 ml	0.0 ml	2.0 ml	50 ml

6.12 **Calibration Curve analysis**

6.12.1 Pour each 50 ml calibration stock solution into a separate, clean 100 ml beaker.

6.12.2 Starting with the lowest standard, immerse both electrodes into the beaker containing the calibration solution. Place a magnetic stirring bar in the solution. Stir the solution and allow the electrode reading to stabilize. Record the mV value on the *Perchlorate Analysis Record*.

6.12.3 Plot the point on a graph of "mV" versus "ppm concentration".

6.12.4 Repeat after every 10 field samples.

6.13 **Sample Analysis**

6.13.1 Pipette **5mL** of sample solution from Step 6.2 into a 50mL volumetric flask.

6.13.2 Add **2mL** of **2M Ammonium Sulfate** solution.

6.13.3 Fill to the 50mL volume mark with distilled water and shake or swirl to mix.

6.13.4 Transfer to a 100mL beaker. Add a magnetic stir bar and immerse both electrodes into the solution. Spin the bar.

6.13.5 Allow the electrode reading to stabilize. Record the mV reading on the *Perchlorate Analysis Record*.

6.13.6 Rinse the electrodes with distilled water between samples.

6.13.7 Place the meter into the Ion Buffer solution. Record the meter reading of the perchlorates in the *Ion Buffer (Post-Test)* line on the *Perchlorate Analysis Record*.

6.13.8 Rinse the probes with distilled water.

6.13.9 Place the probes into distilled water and record the mV reading in the *Distilled Water Post-Test)* line on the *Perchlorate Analysis Record*.

6.14 **Evaluation of Risk:** Evaluate the concentration of perchlorates in the field samples by comparison to the calibration solution.

6.14.1 **Samples with a concentration of less than <u>500 ppm</u> in the test solution are considered negative for the risk of a fire or explosion hazard.**

6.14.2 If desired, quantify the perchlorate concentration per unit area sampled: Divide the concentration measured (in ppm) by 4 to obtain the total weight of perchlorates in the sample in milligrams. Divide the total weight of perchlorates by the surface area sampled to obtain the total weight per square foot. If the weight of perchlorates is less than 6.25 mg per square foot (equivalent to 500 ppm), then the sample is considered negative for the presence of perchlorates.

6.15 Clean-up of lab equipment

6.15.1 Dilute reagents and field sample solutions with tap water and discharge to sink. Flush the sink with water for 3 minutes.

6.15.2 Wash glassware with detergent. Rinse glassware thoroughly with tap water. Triple rinse with distilled water. Air Dry.

6.15.3 Thoroughly wipe up any spilled Perchloric acid on the counter top and equipment with a **wet** paper towel. Thoroughly rinse and wring out the paper towel in the sink three times. Dispose of the paper towel in trash. Flush the sink with water for 3 minutes.

6.15.4 Rinse the outsides of the electrodes in distilled water. Store the electrodes in distilled water, covered in a manner to prevent evaporation of the water.

7.0 Implementation and Training

7.1 **Qualification Criteria:** Only persons who have demonstrated competency in performing this test, to the satisfaction of the SHSD IH Group Leader or designee will be qualified to perform this test. The qualification criteria to perform this procedure are:

7.1.1 Knowledge of industrial hygiene practice (awareness level).

7.1.2 Specific knowledge of this procedure.

7.1.3 Demonstrated competency in performing this test via:

- Visual observation of the sample wiping technique and/or analysis procedure.
- Ability to answer questions on the sampling and analysis procedure and chain of custody of the sample during sampling and transportation.
- Knowledge of the appropriate personal protective equipment for the hazards of this particular type of sampling.

7.2 **Qualification Frequency & Record-keeping:** The SHSD IH Group Leader, or designee, will qualify SHSD IHG personnel to use this procedure. Personnel shall be re-qualified at a frequency not to exceed three years, provided there is no break in the work assignment that utilizes this procedure.

8.0 References

8.1 ***Perchloric Acid Contaminated Hood Decontamination Procedure Manual*, Oak Ridge National Laboratory, Oak Ridge, TN, 1993.**

8.2 **Orion Research Instruction Manual for the Perchlorate Ion Electrode, 1990.**

9.0 Attachments

9.1 **Perchlorate Analysis Record**
9.2 **Field Survey Form**
9.3 **Qualification: Job Performance Measure**

BROOKHAVEN NATIONAL LABORATORY Safety & Health Services Division **INDUSTRIAL HYGIENE GROUP** Standard Operating Procedure	NUMBER **IH75200** REVISION **Final Rev 2**
SUBJECT: INSTRUMENT OPERATION: **Perchlorate and Perchloric Acid Sampling and Analysis Procedure**	DATE **02/01/06** PAGE **11** OF 11

10.0 Documentation

Document Development and Revision Control Tracking

PREPARED BY: *(Signature and date on file)* **A. Sells & R. Selvey** **Date 03/01/00**	**REVIEWED BY:** *(Signature and date on file)* **R. Selvey** SHSD IH Group **Date 09/27/01**	**APPROVED BY:** *(Signature and date on file)* **R. Selvey** SHSD IH Group Leader **Date 09/28/01**
ESH Coordinator/ Date: *none*	Work Coordinator/ Date: *none*	SHSD Manager / Date *none*
QA Representative / Date: *none*	Training Coordinator / Date: *none*	Filing Code: **IH52**
Facility Support Rep. / Date: *none*	Environ. Compliance Rep. / Date: *none*	Effective Date: **09/28/01**
ISM Review - Hazard Categorization ☐ High ☒ Moderate ☐ Low/Skill of the craft	Validation: ☒ Formal Walkthrough ☐ Desk Top Review ☐ SME Review Name / Date:	Implementation: Training Completed: Tracked in BTMS Procedure posted on Web: 02/01/06 Hard Copy files updated: 02/01/06

Revision Log

Purpose: ☐ Temporary Change ☐ Change in Scope ☐ Periodic review ☒ Clarify/enhance procedural controls

Changed resulting from: ☐ Environmental impacts ☐ Federal, State and/or Local requirements ☐ Corrective/preventive actions to non-conformances ☒ none of the above

Section/page and Description of change: Revise format in Section 7. Add ballistic gear to Section5. Changes to field sampling in Section 6 including better description of sampling locations. Addition of date and name to Attachment 9.1.

(signature on file) 03/12/03 Robert Selvey SME Reviewer/Date:	Reviewer/Date:	Reviewer/Date:

Purpose: ☐ Temporary Change ☐ Change in Scope ☐ Periodic review ☐ Clarify/enhance procedural controls

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Section/page and Description of change: Minor changes to Section 7. Minor format changes to Equipment section.

(signature on file) R. Selvey 02/01/06 SME Reviewer/Date:	Reviewer/Date:	Reviewer/Date:

Perchlorate Analysis Record

Date:	**Analysis By:**

Sample ID	Meter Reading (mV)	Perchlorate Concentration
Distilled Water (Pre-Test)		**0**
Ion Buffer (Pre-Test)		**0**
Calibration Standards		
Standard 20 ppm		**20**
Standard 200 ppm		**200**
Standard 400 ppm		**400**
Standard 2000 ppm		**2000**
Field Samples		
1		
2		
3		
4		
5		
6		
7		
8		
9		
10		
Distilled Water (Post Test)		**0**
Ion Buffer (Post-Test)		**0**

Perchlorate Field Sampling form

Date:	**Sample By:**

Building:	**Room:**	**Location:**
Source/Operation Description:		

Sample ID #	Specific Sample Location
1	
2	
3	
4	
5	
6	
7	
8	
9	

BROOKHAVEN NATIONAL LABORATORY

HP-IHP-75200

Environmental, Safety, Health & Quality Directorate
SHSD Industrial Hygiene

Perchlorate and Perchloric Acid Sampling & Analysis
Job Performance Measure (JPM) Completion Certificate

Candidate's Name	**Life Number:**
Qualification for: ____**Field Sampling Only** ____**Lab Analysis Only** ____**Both Field and Lab work**	

Practical Skill Evaluation: Field Sampling

Criteria	**Qualifying Performance Standard**	Unsatis factory	Reco vered	Satisf-actory
1. Hazard Analysis	Understands the need to perform a hazard analysis of the area and potential exposure to the self as sampler and workers in the area.			
2. Personal Protective Equipment	Understands the need to be aware of the potential surface contamination, airborne levels of contaminants, radiological hazards, and noise hazard. Knows how to determine the need for PPE.			
3. Sampling Equipment	Knows where equipment needed for the procedure is located and how to properly sign it out.			
4. Measurement of hazard	Knows how to properly take a sample to avoid an uncontrolled reaction and injury self			
	Knows the technique to lift the highest possible percentage of potential Perchlorates from the surface sampled			
	Knows where to take sample to collect the highest possible sample concentration			
5. Documentation	Demonstrates correctly filling out IH forms, transfers appropriate info to IH databases, and prepares an evaluation assessment report.			

Lab Analysis Practical Skill Evaluation: Demonstration of Methodology

Criteria	**Qualifying Performance Standard**	Unsatis factory	Reco vered	Satisf-actory
1. Hazard Analysis	Understands the hazard of the Perchloric acid stored to make standards & used in the analysis and potential exposure to the self as sampler and workers in the area and the explosion hazard.			
2. Personal Protective Equipment	Understands the need to be aware of the potential surface contamination and radiological hazards on submitted samples. Knows the need for PPE.			
3. Sampling Equipment	Knows where equipment needed for the procedure is located and how to properly operate it.			
4. Calibration	Demonstrates the proper set up of the calibration curve with standards.			
5. Measurement of Perchlorates in samples	Knows how to properly prepare field samples with the AMS solution.			
	Knows how to properly measure field samples with the conductivity meter.			
	Knows how to properly determine the concentration of Perchlorates in the field samples by comparison to the calibration curve.			
6. Documentation	Demonstrates correctly filling out IH forms, transfers appropriate info to IH databases, and prepares an evaluation assessment report.			

I accept the responsibility for performing this task as demonstrated within this JPM and the corresponding SOP.

Candidate Signature:	**Date:**

I certify the candidate has satisfactorily performed each of the above listed steps and is capable of performing the task unsupervised.

Evaluator Signature:	**Date:**